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REMARKS

Claims 1-3, 5, 8-10, 12-17 and 19-34 are now in the application. Claim 1 has been amended to recite "not more than 1.3" in place of " less than 1.8". Support for this amendment can be found on page 8, line 33 of the specification. The amendment to claim 1 does not introduce any new matter.

Claims 1-3, 5, 13-20, 22, 23 and 34 were rejected under 35 USC 102(b) as being anticipated by or, in the alternative, as being obvious over US Patent 5,604,268 to Randen et al. (hereinafter also referred to as "Randen"). Randen does not anticipate and does not render obvious claims 1-3, 5, 13-20, 22, 23 and 34.

Claim 1, as amended, now recites a vinyl polymer having a ratio Mw/Mn of not more than 1.3. However, by using the chain transfer agent disclosed by Randen, it is not possible to prepare a vinyl polymer having a ratio Mw/Mn of not more than 1.3.

This is evidenced by Matyjaszewski et al. HANDBOOK OF RADICAL POLYMERIZATION, Wiley-Interscience, 2002, pages 370-373 (copy attached). On page 373, lines 3-10 of the attached document, it is described that for conventional radical polymerization including transfer agent method, the lowest polydispersity is Mw/Mn = 1.5. This description supports the disclosure of US 4,593,081 (also referred to on page 7, lines 10-11 of the Office Action), in which the lowest Mw/Mn value is 1.48 among all of the disclosed values.

Thus, it is clear that the chain transfer agent cannot give any vinyl polymer having a ratio Mw/Mn of not more than 1.3

On page 7 of the Office Action, the Examiner states that only in specific examples the use of a chain transfer agent is disclosed, wherein the general teaching does not make the selection of a chain transfer agent mandatory. However, the polymerization suggested in Randen is only the chain transfer agent method, which cannot give any vinyl polymer having a ratio

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Mw/Mn of not more than 1.3. Moreover, no other polymerization method is disclosed by Randen.

Hence, one can reasonably conclude that Randen fails to disclose any vinyl polymer having a ratio Mw/Mn of not more than 1.3. Also, see page 10, lines 15-23 of the instant specification.

Further, in view of the fact that the chain transfer agent method suggested in Randen cannot give a vinyl polymer having a ratio Mw/Mn of not more than 1.3, the claimed polymer is not obvious over Randen.

Therefore, amended claim 1, and claims dependent therefrom are not anticipated by, and are not obvious over Randen.

Claims 6, 8-10, 21 and 30-34 were rejected under 35 USC 103(a) as being unpatentable over US Patent 5,807,938 to Matyaszewski or over Randen in combination with Matyaszewski.

Matyaszewski alone and Randen in combination with Matyaszewski fail to render obvious claims 6, 8-10, 21 and 30-34. The above discussion of Randen is incorporated herein by reference. With respect to claim 6, it has been cancelled. As far as Matyaszewski alone is concerned, this rejection has been overcome since claim 1 includes recitations from prior claim 18 except it recites "not more than 1.3" instead of "less than 1.8", which was not previously rejected over Matyaszewski and also includes recitations that are equivalent to that of claim 4, which was not previously rejected over Matyaszewski.

Moreover, Matyaszewski does not overcome the above-discussed deficiencies of Randen with respect to rendering unpatentable the present claims. Matyaszewski fails to even remotely suggest a vinyl polymer having a Mw/Mn of not more than 1.3.

Claims 19 and 24-32 were rejected under 35 USC 103(a) as being unpatentable over Randen or Matyaszewski in view of US Patent 5,381,735 to Fifield.

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The above references fail to render unpatentable claims 19 and 24-32. The above discussions of Randen and Matyaszewski are incorporated herein by reference. Fifield fails to overcome the above-discussed deficiencies of Randen and Matyaszewski with respect to rendering unpatentable the present invention. Fifield was merely relied upon for disclosure of photopolymerizable compositions containing a photopolymerizable material having ehtylenically unsaturated bonds and having olefinic bonds at the termini of the chain which are further polymerized by use of actinic radiation.

The cited references fail to anticipate the present invention. In particular, anticipation requires the disclosure, in a prior art reference, of each and every recitation as set forth in the claims. *See Titanium Metals Corp. v. Banner*, 227 USPQ 773 (Fed. Cir. 1985), *Orthokinetics, Inc. v. Safety Travel Chairs, Inc.*, 1 USPQ2d 1081 (Fed. Cir. 1986), and *Akzo N.V. v. U.S. International Trade Commissioner*, 1 USPQ2d 1241 (Fed. Cir. 1986).

There must be no difference between the claimed invention and reference disclosure for an anticipation rejection under 35 USC 102. *See Scripps Clinic and Research Foundation v. Genetech, Inc.*, 18 USPQ2d 1001 (CAFC 1991) and *Studiengesellschaft Kohle GmbH v. Dart Industries*, 220 USPQ 841 (CAFC 1984).

To the extent that the Examiner is relying upon inherency, this is improper. Inherency requires that the recited results or structure must necessarily be obtained not merely that it might be achieved. *See Electra Medical Systems S.A. v. Cooper Life Sciences, Inc.*, 32 USPQ2d 1017 (Fed. Cir. 1994); *In re: Oelrich*, 212 USPQ 323 (CCPA 1981) and *In re Robertson*, 49 USPQ2d 1949 (Fed. Cir. 1999).

The mere fact that cited art may be modified in the manner suggested in the office action does not make this modification obvious, unless the cited art suggest the desirability of the modification. No such suggestion appears in the cited art in this matter. The Examiner's attention is kindly directed to *In re Lee*, 61 USPQ2d 1430 (Fed. Cir. 2002), *In re Dembiczak et al.*, 50 USPQ 2d 1614 (Fed. Cir. 1999), *In re Gordon*, 221 USPQ 1125 (Fed. Cir. 1984), *In re*

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Laskowski, 10 USPQ2d 1397 (Fed. Cir. 1989) and *In re Fritch*, 23 USPQ2d 1780 (Fed. Cir. 1992).

In Dembiczak et al, supra, the Court at 1617 stated: "Our case law makes clear that the best defense against the subtle but powerful attraction of a hindsight-based obviousness analysis is rigorous application of the requirement for a showing of the teaching or motivation to combine prior art references. See, e.g., C.R. Bard, Inc. v. M3 Sys., Inc., 157 F.3d 1340, 1352, 48 USPQ2d, 1225, 1232 (Fed. Cir. 1998) (describing 'teaching or suggestion motivation [to combine]' as in 'essential evidentiary component of an obviousness holding'), in re Rouffet, 149 F.3d 1350, 1359, 47 USPQ2d 1453, 1459 (Fed. Cir. 1998) ('the Board must identify specifically...the reasons one of ordinary skill in the art would have been motivated to select the references and combine them');...".

Also, the cited art lacks the necessary direction or incentive to those of ordinary skill in the art to render the rejection under 35 USC 103 sustainable. The cited art fails to provide the degree of predictability of success of achieving the properties attainable by the present invention needed to sustain a rejection under 35 USC 103. See *Diversitech Corp. V. Century Steps, Inc.*, 7 USPQ2d 1315 (Fed. Cir. 1998), *In re Mercier*, 185 USPQ 774 (CCPA 1975) and *In re Naylor*, 152 USPQ 106 (CCPA 1966).

Moreover, the properties of the subject matter and improvements which are inherent in the claimed subject matter and disclosed in the specification are to be considered when evaluating the question of obviousness under 35 USC 103. See *Gillette Co. v. S.C. Johnson & Son, Inc.*, 16 USPQ2d 1923 (Fed. Cir. 1990), *In re Antonie*, 195, USPQ 6 (CCPA 1977), *In re Estes*, 164 USPQ 519 (CCPA 1970), and *In re Papesch*, 137 USPQ 43 (CCPA 1963).

No property can be ignored in determining patentability and comparing the claimed invention to the cited art. Along these lines, see *In re Papesch, supra, In re Burt et al*, 148 USPQ 548 (CCPA 1966), *In re Ward*, 141 USPQ 227 (CCPA 1964), and *In re Cescon*, 177 USPQ 264 (CCPA 1973).

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In view of the above, consideration and allowance are, therefore, respectfully solicited.

In the event that the Examiner believes an interview might serve to advance the prosecution of this application in any way, the undersigned attorney is available at the telephone number noted below.

The Commissioner is hereby authorized to charge any fees or credit any overpayment associated with this communication including any extension fees to Deposit Account No. 22-0185.

Dated: 7-9-04

Respectfully submitted,

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HANDBOOK OF RADICAL POLYMERIZATION

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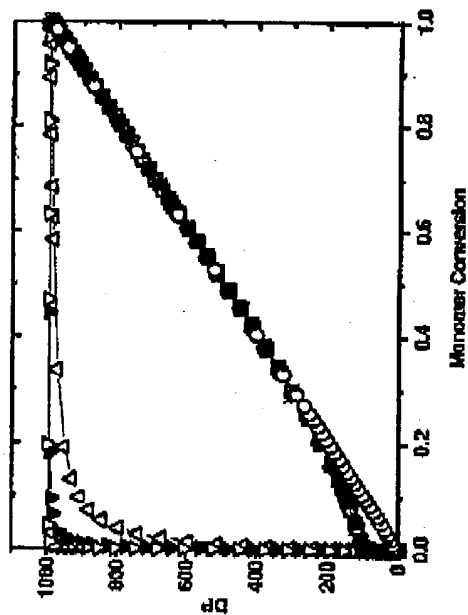*University of New South Wales, Sydney, Australia*

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Figure 8.7 Dependence of degrees of polymerizations on conversion for systems with slow exchange and with the ratio of $[I]_0 k_p/([X]k_d) = 0.01$ (O), 0.1 (variable k_a: ◇ ■ □) and 1 (variable k_a: △ ▲ ▽).

using either a higher concentration of deactivator or a more reactive deactivator (higher k_{da}). The rate of activation does not affect the polydispersities when they are plotted against conversion (various filled and open symbols). However, when polydispersities are plotted against the reaction time, they scale well with the rate constants of activation.[22] As explained in much greater details in Chapter 9, using such a kinetic analysis, the evolution of polydispersities with time depends only on k_a, but is totally independent of k_{da}.

When slow exchange is the only reason for the broadening MWD, its rate simply correlates with polydispersity. If chain breaking reactions (transfer, termination, etc.) are additionally present, then the polydispersity increases with conversion. This may lead to a certain "window" of degree of polymerization at which well-defined polymers can be prepared. Thus, at a low range of MW, the polydispersities may be higher than in ideal systems because of slow exchange (or slow initiation), but they may be also higher at high conversion due to progressively more noticeable side reactions.

Figure 8.7 shows the effect of slow deactivation on evolution of DP with conversion. If deactivation is relatively fast, DP increases linearly with conversion. However, for slow deactivation, such as when $([I]_0 k_p)/([X]k_{da}) = 1$ (triangles), DP is much higher than predicted, and is only slightly affected by the rate constants of activation.

Control of both DP and polydispersity improves with either faster deactivation or lower initiator concentration, when longer chains are targeted. This occurs until chain breaking reactions start to affect DP and polydispersity. In some systems, slow exchange may lead to polymers with even higher polydispersities, $M_w/M_n > 2$.

This may happen even in systems with an insignificant contribution of chain breaking reactions when exchange is slow enough.

For the degenerative transfer process a deactivator also generates chains (it may also be considered as an initiator) and therefore simplifies to:

$$\frac{M_w}{M_n} = 1 + k_p/k_{exch}\left(\frac{2}{p} - 1\right) \tag{3}$$

Thus, polydispersity depend only on k_p/k_{exch} and conversion. However, the slow monomer addition may further reduce the polydispersity as demonstrated in addition–fragmentation reactions.[23]

8.3.3 Slow Initiation

Fast initiation is a prerequisite for the synthesis of polymers with degrees of polymerization predetermined by $\Delta[M]/[I]_0$ ratios. In systems without exchange and without chain breaking reactions, the upper polydispersity limit is $M_w/M_n < 1.35$, as a result of slow addition.[24] When slow initiation occurs and growing chains exist in dormant and active forms, polydispersity can be significantly higher. Slow initiation leads to slower polymerization, usually accompanied by induction periods, and to molecular weights higher than predicted by $\Delta[M]/[I]_0$. The effect of slow initiation is especially easy to notice when synthesizing low molar mass polymers. In degenerative transfer processes (e.g., RAFT), the aforementioned effect of slow initiation on MW and polydispersities can be translated to the slow consumption of the original transfer agent.

8.3.4 Other Factors

Control of molecular weights and polydispersities may be additionally affected by the reversibility of propagation and by inhomogeneity of the system. Heterogeneous catalytic systems may also lead to higher polydispersities. However, if the catalyst acts via activation/deactivation, then heterogeneity should not affect polydispersities unless exchange reactions are too slow (e.g., concentration of deactivator X or XY is too low). Poor solubility of the initiator (e.g., macroinitiator for block copolymerization) or a growing polymer will also lead to higher polydispersities.

8.4 TYPICAL FEATURES OF CONVENTIONAL FREE-RADICAL POLYMERIZATION

In this section, the conventional free-radical polymerization (RP) is briefly summarized in order to compare it with LRP. Free-radical polymerization has been known for more than sixty years. The basic theory and comprehension of radical polymerization was established by the 1950s.[13] It included a basic understanding of the mechanism of the process, encompassing the chemistry and kinetics of the

transfer has no effect on kinetics, only on molecular weights. If reinitiation is slow, then some retardation/inhibition may occur.

Polymers with molecular weights in the range of $M_n \approx 100,000$ are formed. However, in the presence of transfer agents, it is possible to prepare polymers with much lower M_n. It is also possible to prepare polymers with $M_n > 10^6$, but this is often a difficult task because of transfer and termination reactions between growing radicals. The lowest polydispersity for conventional radical polymerization is $M_w/M_n = 1.5$, which is attainable at low conversions and for termination by coupling. However, in most systems polydispersities exceed $M_w/M_n > 2$, especially at higher conversions. Typically, overall kinetics is first-order with respect to monomer and half-order with respect to initiator. The overall rate constant of polymerization is a function of the efficiency of initiation (f), the rate constant of initiation (k_i), propagation (k_p), and termination (k_t). All of these rate constants are also very important for LRP processes since control in LRP depends strongly on the delicate balance between various kinetic parameters.

1.5 LIMITATIONS OF CONVENTIONAL RADICAL POLYMERIZATION

As stated before, the main disadvantage of RP in comparison with ionic polymerization are the diffusion-controlled termination reactions between growing radicals. However, since termination is second-order, whereas propagation is first-order, with respect to growing radical concentration, by keeping the concentration of radicals very low, it is possible to build a polymer chain of appropriate molecular weight. In conventional systems this is accomplished by continuous slow initiation. Often when >90% of monomer is converted to polymer, only <20% of initiator has been consumed. Slow and continuous initiation prevents synthesis of well-defined polymers with degrees of polymerization predetermined by the ratio of concentrations of the converted monomer to the introduced initiator, with low polydispersities, with controlled topologies (stars, combs) and compositions (blocks, grafts, gradients).

The typical lifetime of a propagating chain is very short, in the range of 1 s. During that time approximately 1000 monomer units are added to the generated radicals prior to termination. Thus, macromolecular engineering is not feasible, because it is difficult during 1 s to add a sequence of another monomer to form block copolymer, or add a special terminating agent to produce end-functional polymers and so on. A hypothetical extension of the lifetime of growing radicals would require a considerable slow down of the polymerization. In such a regime, however, the molecular weights would become limited by transfer rather than by termination and remains poorly controlled.

There are two methods in RP that can provide polymers with lower molecular weights. The first method requires larger amounts of initiator and may be accompanied by a significant and uncontrolled increase of the polymerization rate. The second approach is based on transfer agents and can provide polymers, oligomers,

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elementary reactions involved, determination of the corresponding absolute rate constants, the structure and concentrations of the growing species, and a correlation of the structure of the involved reagents with their reactivities. Since that time, significant progress has been made and a more detailed comprehensive understanding of RP has been presented in the preceding seven chapters.

Nearly all compounds with C=C bonds can be either homopolymerized or copolymerized via a radical mechanism. They should fulfill two basic requirements: thermodynamic polymerizability and kinetic feasibility. The former indicates sufficient negative free energy of polymerization and the latter sufficient reactivity of monomer, stability of the derived free-radical, and a low proportion of side reactions. Most monosubstituted alkenes polymerize radically; some disubstituted alkenes either homopolymerize (methacrylates) or copolymerize (isobutene, maleic anhydride). Isobutene and α-olefins do not provide high molecular weight polymers radically since they propagate slowly and participate in transfer reactions. However, copolymerization of these monomers with electron-poor monomers is successful. Radical polymerization of unprotected hydroxyethyl (meth)acrylates, (meth)acrylic acid, and some amino derivatives lead to high molecular weight polymers, in contrast to ionic systems because radicals are tolerant to protons on heteroatoms. Monomers can be polymerized in bulk, in organic solvents and also in aqueous suspension/emulsion. The choice of solvent is limited only by potential transfer reactions.

Radical polymerization consists of four basic elementary steps: initiation, propagation, termination, and transfer. Initiation is usually composed of two processes: generation of a primary initiating radicals and reaction of these radicals with monomer. The former reaction is much slower than the latter, and it is rate determining, with typical values of $k_d \approx 10^{-5} s^{-1}$ and $k_i > 10^5 M^{-1} s^{-1}$. Typical initiators (peroxides, diazo derivatives, redox systems, organometallics, and photolabile compounds) are used at concentrations between 1 and 0.01 mol%. The reaction temperature is correlated with the initiator structure in such a way that 50% of the initiator is typically decomposed within 10 h. During that time more than 95% monomer conversion is often reached.

Propagation occurs by the repetitive addition of the growing radical to the double bond. It is considered to be chain-length-independent, with typical values of $k_p \approx 10^{3\pm1} M^{-1} s^{-1}$. The concentration of the propagating free radicals is established by balancing the rates of initiation and termination and is equal to $[P^\cdot] \approx 10^{-8\pm1} M$).

Termination between two growing radicals can occur by either coupling (k_{tc}) or disproportionation (k_{td}) with rate constants approaching the diffusion controlled limit, $k_t > 10^7 M^{-1} s^{-1}$. Rate coefficients of termination are chain length and conversion dependent. If termination by coupling dominates, then polymers with higher molecular weights and lower polydispersities are formed.

The fourth elementary reaction is transfer. Transfer can occur to monomer or to polymer. In the latter case, the M_w value is not affected, but polydispersities increase as a result of formation of branched and in some cases crosslinked polymers. Transfer can also occur to a transfer agent (TA). Typically, reinitiation (k_{rinit}) is fast, and

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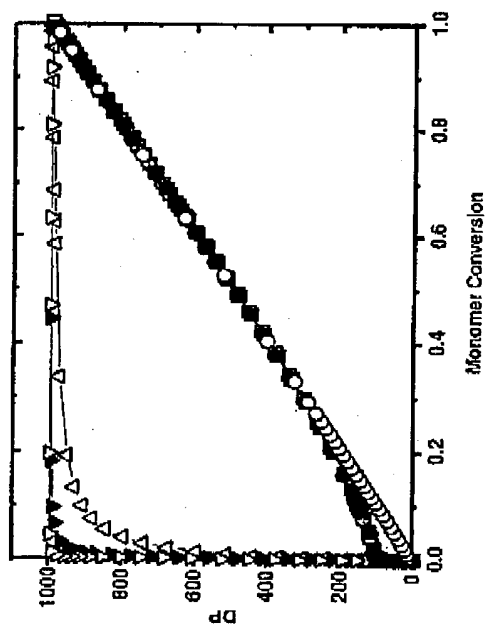370 GENERAL CONCEPTS AND HISTORY OF LIVING RADICAL POLYMERIZATION

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transfer has no effect on kinetics, only on molecular weights. If reinitiation is slow, then some retardation/inhibition may occur.

Polymers with molecular weights in the range of $M_n \approx 100,000$ are formed. However, in the presence of transfer agents, it is possible to prepare polymers with much lower M_n. It is also possible to prepare polymers with $M_n > 10^6$, but this is often a difficult task because of transfer and termination reactions between growing radicals. The lowest polydispersity for conventional radical polymerization is $M_w/M_n = 1.5$, which is attainable at low conversions and for termination by coupling. However, in most systems polydispersities exceed $M_w/M_n > 2$, especially at higher conversions. Typically, overall kinetics is first-order with respect to monomer and half-order with respect to initiator. The overall rate constant of polymerization is a function of the efficiency of initiation (f), the rate constant of initiation (k_d), propagation (k_p), and termination (k_t). All of these rate constants are also very important for LRP processes since control in LRP depends strongly on the delicate balance between various kinetic parameters.

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The typical lifetime of a propagating chain is very short, in the range of 1 s. During that time approximately 1000 monomer units are added to the generated radicals prior to termination. Thus, macromolecular engineering is not feasible, because it is difficult during 1 s to add a sequence of another monomer to form block copolymer, or add a special terminating agent to produce end-functional polymers and so on. A hypothetical extension of the lifetime of growing radicals would require a considerable slow down of the polymerization. In such a regime, however, the molecular weights would become limited by transfer rather than by termination and remains poorly controlled.

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